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(71) Applicant  
**Shell Internationale Research Maatschappij B.V.**  
**(Incorporated in the Netherlands)**  
**Carel van Bylandtlaan 30, The Hague, Netherlands**

(72) Inventors  
**Seetha Coleman Kammula**  
**Richard Lewin Wife**

(74) Agent and/or Address for Service  
**K R I Hunter**  
**4 York Road, London, SE1 7NA, United Kingdom**

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(54) **Process for producing reinforced copolymer compositions**

(57) A copolymerization process for preparing alternating copolymers of carbon monoxide and an olefinically unsaturated compound with a catalyst comprising palladium characterized in that the copolymerization is effected in the presence of a fibre reinforcement material.

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PROCESS FOR PRODUCING REINFORCED  
COPOLYMER COMPOSITIONS

5 The present invention is concerned with fibre reinforced copolymer compositions. The relevant copolymers are those having the alternating polyketone structure  $\text{---}[\text{A-CO}]_n\text{---}$  in which n is at least 10 and A is a unit derived from an olefinically unsaturated compound, e.g. ethene or propene. The term "copolymer" also includes terpolymers in which different units are present, e.g. both ethene and butene or propene and pentene, hexene or styrene.

10 The relevant alternating copolymers and suitable methods of preparation are known per se, e.g. from EP-A-121,965 and 181,014, disclosing homogeneous palladium/bisphosphine catalyst systems. Whilst such copolymers have attractive physical and mechanical properties such as yield stress, tensile strength, impact strength and flexural modulus, all of these properties may be improved significantly by incorporating reinforcing fibres, e.g. glass  
15 fibres, or other fibrous materials into the copolymer matrix. However, the Applicants have found that the envisaged improvements fall short of expectation and in further research the Applicants have established that this disappointing performance is related to inadequate adherence of the fibre reinforcement materials to the  
20 copolymer matrix.

The problem underlying this invention is therefore the need for effecting acceptable adherence of reinforcement fibre to the relevant copolymers.

25 Surprisingly, the Applicants have found that this problem may be solved by carrying out the preparation of the relevant copolymers, i.e. the copolymerization per se of carbon monoxide and olefinically unsaturated compound, in the presence of fibre reinforcement material.

The present invention relates to a copolymerization process for preparing alternating copolymers of carbon monoxide and an olefinically unsaturated compound with a catalyst comprising palladium characterized in that the copolymerization is effected in the presence of a fibre reinforcement material.

Preferred copolymerization methods are selected from liquid phase slurry copolymerization methods and from gas phase copolymerization processes.

Liquid phase, slurry copolymerization processes with homogeneous palladium bisphosphine catalyst systems which can be used for carrying out the process of this invention may be any one of the process known from the prior art, including but not limited to EP-A-121,965; 181,014; 222,454; 235,866; 239,145; 246,683; 245,893; 253,416; 254,343 and 229,408. Gas phase copolymerization is known from EP-A-248,483. The copolymerization methods per se form no part of this invention, which basically is directed to carrying out the copolymerization in the presence of reinforcing fibres. When applying a liquid phase method, the use of solvents for both the catalyst system and the copolymer produced is not envisaged. The solvent must be selected from those in which the catalyst system is readily soluble but in which the copolymer produced is not soluble, in the prior art methods the latter therefore precipitates from the liquid phase, usually in the form of a fine, fluffy powder, during production. Liquid phase slurry copolymerization represents the most preferred mode for carrying out the process of this invention.

Preferred catalyst compositions comprise:

- a) a palladium compound,
- b) a bisphosphine bidentate ligand, and
- c) a strong acid, i.e. an acid with a pKa of less than 4, preferably less than 2, provided this acid is not a hydrohalogenic acid.

Further activity enhancing compounds may be included in the catalyst compositions e.g. 1,4-benzoquinone or 1,4-naphthoquinone

as further catalyst component d). Very attractive polymerization rates are found with ortho alkoxy substituted bis-aryl phosphine bidentate ligands.

5 All conditions to be observed during copolymerization per se, such as total pressure, partial pressure of carbon monoxide and olefin, temperature, time, catalyst component concentration and components a:b:c molar ratios are as indicated in the EP-patent applications quoted hereinbefore and therefore need not to be repeated in detail herein.

10 Suitable reinforcing fibres may be selected from melt-spun commodity thermoplastic or engineering thermoplastic fibres, such as polyethene, polypropene or polyamide fibres.

15 A special group includes polyaramide, gel-spun polyethene and carbon fibres. Most preferred are glass fibres. Fibrous reinforcing materials include shredded wood pulp, fibrillated thermoplastic film and similar thermoplastic products. Non-woven fabrics may also be employed.

20 Fibre length can in principle range from 3 mm to unlimited (continuous fibre) albeit lengths of up to 250 mm, even better up to 100 mm are preferred. Fibre aspect ratio is preferably in between 1000 and 10000 but higher and lower values can be applied for special purpose applications.

The precipitation of the copolymer during its production in the copolymerization reactor covers the fibres with a solid coating  
25 of crystalline copolymer. Little or no copolymer is precipitated elsewhere. The thickness of the coating on the fibres is controlled by proper selection of the copolymerization process parameters, in particular time and temperature and dependent upon the desired mass/mass ratio of reinforcing fibres to copolymer matrix in the  
30 desired final articles of manufacture such as laminates, film, sheets, bottles, tubes, piping and injection-moulded articles of intricate shape.

35 Upon the withdrawal of the copolymer coated fibres from the copolymerization reactor and removal of liquid phase by simple techniques, e.g. evaporation of volatile solvent at room

temperature or drying by heating, the fibres can be easily processed into finished articles of manufacture by conventional processing technology, preferably blow-moulding, extrusion, co-extrusion, solid phase pressure forming, injection-moulding, compression-moulding or pultrusion.

During such processing various additives, such as fillers, antioxidants, U.V.-stabilizers, pigments, dyes, lubricants or other processing aids may be incorporated into the desired composite materials and final articles of manufacture.

#### EXAMPLES

##### Copolymerization general

Into a 500 ml volume pressure vessel 250 ml of dry, degassed methanol was introduced. Carbon monoxide/ethylene gas mixtures in a 1:1 molar ratio were introduced such that a pressure of 55 bar was reached. After bringing the reactor temperature to 90 °C a catalyst solution comprising palladium acetate,

1,3-di(di-orthomethoxyphenylphosphino)propane and trifluoroacetic acid in a molar ratio of 1:1.2:20 dissolved in a mixture of 45 ml of methanol and 15 ml of toluene was injected. When most of the gaseous reactants had been consumed, the CO/ethylene copolymer product was filtered, weighed and dried.

The procedure for gas-phase copolymerization is the same as set out above, apart from the omission of the injection of 250 ml portion of solvent.

##### Copolymerization in the presence of glass fibres

Polymerizations in the presence of glass fibres were conducted following the above procedure with the exception that the designated amounts of glass fibres (Table 1) were added to the methanol solvent prior to introducing the reactant gases. The products were washed and yields are presented in Table 1. Product yields depended on the type of glass fibre/coating agent.

Table 1

Glass Fibre	Fibre %w	Solvent	[Pd], mg/l	Time, hrs	Copolymer yield kg/g.Pd
SILENKA <sup>a)</sup>					
1 8047	20	A	1	16	18
SILENKA					
2 8047	10	B	2	2½	2.66
SILENKA <sup>b)</sup>					
3 8044	10	A	1	16	0.17
SILENKA					
4 8044	10	none	3	18	11
SILENKA					
5 8047	5	A	2	4	27
MICROLITH					
GLASS FLEECE <sup>c)</sup>	2.011	none	1	65 <sup>d)</sup>	60
7 None	-	A	1	16	19.5

A = methanol

B = methylethylketone

a) coated with polycarbonate compatible sizing agent.

b) coated with nylon compatible sizing agent.

c) a non-woven monofilament fleece.

d) copolymerization temperature was 67 °C.

5 Upon visual inspection under the microscope of the products withdrawn from the copolymerization reactor it was established that in each experiment except run 7 at least 80 %w of the copolymer was deposited in the form of fibrous crystallites adhering to the reinforcing fibres, thus forming a continuous coating on the fibres.

10 The copolymers produced in experiments 6 and 7 were transformed into compression-moulded test specimen, and copolymer from run 7 was also compression moulded following incorporation of glass reinforcing fibres in the same weight percentage as contained in the copolymer from experiment 6. Determination of the E-modulus yields 10 GPa for fibre reinforced copolymer from experiment 6,

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3.5 GPa for fibre reinforced copolymer from experiment 7 and 1.0 GPa for the non-reinforced copolymer from experiment 7.

The spectacular jump from 3.5 to 10 GPa is an indication of the unexpectedly improved adherence of copolymer to fibre.

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C L A I M S

1. A copolymerization process for preparing alternating copolymers of carbon monoxide and an olefinically unsaturated compound with a catalyst comprising palladium characterized in that the copolymerization is effected in the presence of a fibre reinforcement material.
2. Process as claimed in claim 1 in which fibres having an aspect ratio of 1000 to 10000 are employed.
3. Process as claimed in claim 1 or 2 in which fibres having a length of up to 250 mm, preferably from 3 to 100 mm are employed.
4. Process as claimed in any one of claims 1 to 3 in which glass fibres are employed.
5. Process as claimed in any one of claims 1 to 3 in which the fibres employed are selected from carbon fibres, polyaramide fibres and gel-spun polyethylene fibres.
6. Process as claimed in claim 1 and substantially as hereinbefore described with particular reference to the example.
7. Compression-moulded, injection-moulded, blow-moulded, extruded, coextruded, pultruded or solid phase pressure formed articles of manufacture comprising a polymer composite material characterized in that the polymer composite is an alternating olefin/CO copolymer produced by a process as claimed in any one of claims 1 to 6.